Critical Potentials and Currents Relating to Local Oxide Behavior on Aluminum Microelectrodes

F. D. Wall, M. A. Martinez
Sandia National Labs
P.O. Box 5800
Albuquerque, NM 87185-0888

Pitting potentials of both stainless steel[1,2] and aluminum[3] have been reported to increase as the surface area of the sample is reduced. Such data can be used to infer that the pitting potential is linked to a random distribution of defect sites and as sample size increases the probability of the sample containing a susceptible site will also increase. It also follows that very small samples will contain a reduced population of defects and in the limit may contain a single defective region. Thus, the opportunity exists to use microelectrodes to investigate the electrochemical behavior associated with highly localized failure of an oxide at a single site. The passive currents on microelectrodes can be on the order of nA or pA and will not mask the local current flowing from a flawed site. In this work we use microelectrode samples to probe both the specific electrochemical signatures associated with individual oxide breakdowns, and parameters that can be used to describe stochastic behavior associated with populations of pitting sites.

Experiments performed on 99.99 Al wire electrodes in 50 mMol NaCl have already revealed a qualitative dependence of pitting potential on electrode size (Fig. 1). We will present further data from testing of 500, 250, 100, 50, 25 and 5 μm Al wires and test the ability to predict the behavior of larger electrodes based on the populations of pitting potentials recorded on smaller electrodes.

Galvanodynamic testing of micro-electrodes is being used to describe the local oxide conductivity prior to and during pit initiation. Because the I_{PASS} (total passive current) is so small on microelectrodes, galvanodynamic tests may yield information normally masked on large electrodes. In particular, the average current density can be hundreds or thousands of times higher on small electrodes just before oxide rupture (Fig. 2). We speculate that this difference is due to local "leaks" in the oxide where a defective structure or composition has resulted in higher oxide conductivity. Further work will be used to determine the distributions of critical currents recorded just prior to oxide breakdown. Analyses will also be presented that explore the applicability of Galvele's x*i stability criterion for pit growth[4] to pit initiation.

REFERENCES

1. G. T. Burstein, G. O. Ilevbare, Corrosion Science, Vol. 38, No. 12, pp. 2257-2265 (1996).
2. H. Böhni, T. Suter, A. Schreyer, Electrochimica Acta, Vol. 40, No. 10, 1361-1368 (1995).
3. J. E. Sweitzer, J. R. Scully, R. A. Bley, J. W. P. Hsu, Electrochemical and Solid State Letters, 2 (6) 267-270 (1999).
4. J. R. Galvele, J. Electrochem. Soc., Vol. 123, No. 4, pp. 464-474 (April, 1976).

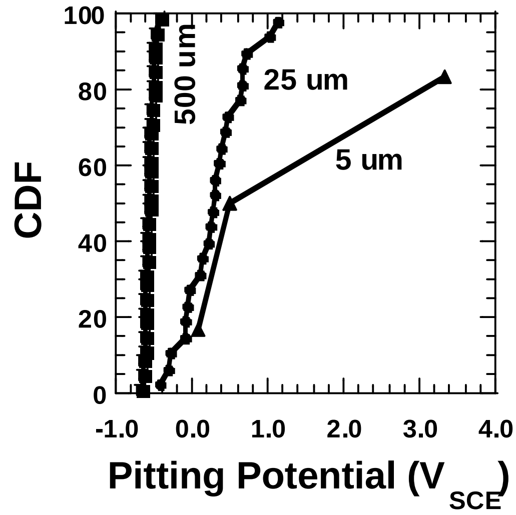

Figure 1. Distributions of aluminum pitting potentials as a function of electrode diameter. Testing was performed in aerated 0.05 M NaCl @ 25°C.

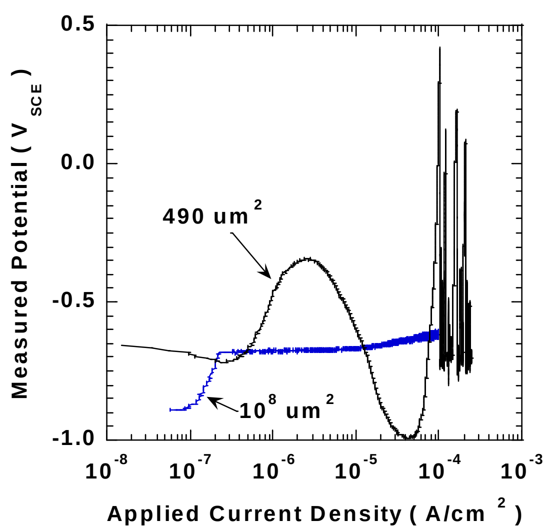

Figure 2. Galvanodynamic testing of pure aluminum as a function of electrode area. Testing was performed in aerated 0.05 M NaCl @ 25°C.